
MODIFICATION
OF POLYMERS

Framed Aromatic Polyurethanes Based on an Anionic Macroinitiator, 4,4'-Diphenylmethane Diisocyanate, and 4,4'-Dihydroxy-2,2-diphenylpropane: Metal-Complex Modification

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Abstract—Metal complexes are prepared from poly(oxyethylene glycol) and iron(III) chloride and studied as modifiers of framed aromatic polyurethanes. The latter polymers are synthesized on the basis of macroinitiators, 4,4'-dihydroxy-2,2-diphenylpropane, and polyisocyanate, which is a mixture of 4,4'-diphenylmethane diisocyanate and its branched derivatives. The interaction of iron(III) chloride with poly(oxyethylene glycol) is accompanied by redox processes that lead to its degradation and partial reduction of Fe(III) to Fe(II). Aromatic polyurethanes are modified in the concentration range of metal complexes from 0.5 to 20%. At a concentration of metal complexes of 4–7%, the polymer shows high mechanical characteristics and excellent thermal stability. The framed structure of aromatic polyurethanes hampers the effective contacts of coordinately bonded Fe atoms that are present in various oxidation states.

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Polyurethanes provide a basis for designing materials with a wide set of performance characteristics [1–4]. Variation in the chemical nature of initial components makes it possible to manufacture both impact-resistant plastics and elastomers. One of the ways to govern the chemical structure and morphology of polyurethanes is based on the use of complexing systems, in which transition-metal atoms play the key role in their synthesis and modification.

It is known [5–11] that the nature of a polymer and transition metals, as well as their ratio and interaction energy, determines the change in the properties of coordinately bonded polymers. When metal complexes are used for the modification or structuring of linear polyurethanes, polymer electrolytes, drivers, sensors, and other devices may be manufactured [12–14]. The use of a flexible-chain component, which manifests a high segmental mobility, for the synthesis of PUs, leads to a high mobility of dissolved metal compounds and, accordingly, to the appearance of ionic conductivity. The domains of rigid blocks, which

serve as reinforcing fillers, contribute to the mechanical strength of polyurethanes prepared using oligo(ether diols) [15–18].

For development of approaches to the synthesis of metal-coordinated polyurethanes, it is of interest to employ open-chain analogs of crown ethers (podands) containing terminal hydroxyl groups. A partial replacement of hydroxyl groups with potassium alcoholate groups entails the appearance of catalytic activity; therefore, the term macroinitiators may be applied to these compounds. As a consequence, the initiation of opening of isocyanate groups via the anionic mechanism and the catalytic effect on the reaction of urethane formation become possible. Podands in turn may be hydrophobic poly(oxypropylene glycols), hydrophilic poly(oxyethylene glycols), or amphiphilic block copolymers of ethylene oxide and propylene oxide. This circumstance may ensure widening of the targeted control over the reactivity of corresponding alcoholates and the supramolecular structure of the related polymers. Another important feature of